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Temporal changes in $\delta^{18}O$ and $\delta^{15}N$ of nitrate nitrogen and H_2O in shallow groundwater: Transit time and nitrate-source implications for an irrigated tract in southern Idaho

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ABSTRACT

Intensive irrigated agriculture in semiarid southern Idaho contributes to nitrate loads in shallow groundwater. To determine the temporal character and source of leached nitrate in the Twin Falls Irrigation Tract, and investigate the soil N cycling process involved, we measured stable isotope ratios of nitrate ($\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3) and water ($\delta^{2}H$-H_2O, $\delta^{18}O$-H_2O) in 1) tunnel drain and irrigation waters during 2003-07, and 2) leachate from incubated urea- and manure-amended soil endmembers. The tunnel water $\delta^{2}H$-H_2O vs. $\delta^{18}O$-H_2O plots showed clear overlap with waters of Milner reservoir, which stores the tract's irrigation water prior to distribution. The $\delta^{18}O$-H_2O time series and a correlation analysis with climate/hydrologic parameters indicated a 20 to 23 month, transit time between the surface and shallow groundwater. The tunnel waters had a mean $\delta^{15}N$-NO_3 of +6.1 ± 0.7‰ (± Std. Dev.) and mean $\delta^{18}O$-NO_3 of −6.1 ± 0.7‰. Decreasing tunnel-water $\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3, and nitrate concentrations in tunnel drains located closer to the Snake R indicate increasing contributions of regional groundwater to shallow groundwater and dilution of the latter's NO_3–N content as proximity to the river increases. Relative to all-other tunnels, water from the two tunnels closest to Snake River were depleted in $\delta^{15}N$-NO_3 (+5.4‰ vs. + 6.3‰) and included a greater contribution of regional groundwater (71% vs. 47%). Nitrate $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 ratios for tunnel waters plotted between those of urea (fixed-N) amended soil (4.6 ± 0.5‰ and −4.9 ± 1.4‰), manure-amended soil (13.4 ± 1.3‰ and −4.4 ± 1.2‰), and regional groundwater endmembers. A dual-isotopic element, three-source, simple linear mixing model indicated that, on average, 1.5X more N is sourced from fertilizer and fixed N than animal waste. The dominant N-cycling process in the system at the scale observed here is the nitrification of NH_4-N derived from applied fertilizer and manure, whereas denitrification has a minor influence.

1. Introduction

Only 40% of nitrogen applied to the world's crops is incorporated into the harvested products worldwide on average; and the resulting excess soil reactive N can cause adverse environmental and human health impacts (Zhang et al., 2015). Agricultural nitrogen use efficiency (NUE) must improve if future global food needs are to be met in a sustainable manner (Zhang et al., 2015). This is also true in the western US, where near optimal light and temperature conditions, combined with generous N and P fertilizer applications, often produce peak yields for irrigated crops.

Since the 1970's, increasing crop yields and the robust growth of a regional dairy industry have resulted in increased fertilizer and dairy manure applications to farm lands in south-central Idaho, and to the Twin Falls Canal Co. (TFCC) irrigation tract in particular (Lentz et al., 2018). Nitrate concentrations in shallow groundwater exiting subsurface tunnel drains in the TFCC tract were sampled on a monthly or bimonthly basis in the late 1960s (Carter et al., 1971), 1999, and 2002–2007 (Lentz et al., 2018). Mean nitrate-N concentrations in shallow groundwater of the tract have increased with time from 3.1 to 5.1 mg L^{-1} (Lentz et al., 2018). These concentrations are small relative to the 119 mg L^{-1} median NO_3-N concentration reported for soil drainage water below local irrigated crops, and the reason for this is not clear.

The source of nitrate contamination in shallow groundwater can be inferred from nitrate concentrations coupled with nitrate ^{15}N and ^{18}O

Abbreviations: ANOVA, Analysis of variance; LMWL, Local meteoric water line; TFCC, Twin Falls Canal Co

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stable isotope contents if nitrate source inputs and end members are known, and transformations of N along flow paths are minimal (Böhlke et al., 2003; Nestler et al., 2011; Xing and Liu, 2016). Transport rates (from which transit times can be inferred) of water from the soil surface to shallow groundwater can be deduced from time series measurements of stable isotopes in recharge water and groundwater sources (Clark and Fritz, 1997; Hunt et al., 2005).

Irrigated cropland is the major source of percolating soil waters in the tract, and agricultural fertilizers and animal wastes are the key contributors to nitrate loading, (Bahr and Carlson, 2000; Holloway et al., 2004; Lentz et al., 2018). During the current study, ammonium or urea fertilizers comprised > 90% of fertilizer applied (Idaho State Dept. Agriculture, 2005), and nitrate concentration in irrigation water is generally < 1% of that in soil percolation water (Lentz et al., 2018). Another potential source of leached nitrate is derived from ammonification and nitrification of N fixed in legume root and crown biomass, particularly alfalfa (*Medicago sativa* L.). Because NH_4-N from alfalfa biomass and urea fertilizer have similar $\delta^{15}N$ (Unkovich, 2013), and both are converted to NO_3 by soil nitrification, nitrate from the two sources is indistinguishable. Thus, N fixed from atmospheric N_2 (inorganic fertilizers and legume biomass) and N from manure provide the dominate N inputs into tract soils.

Several groundwater studies collected a single water sample annually from many of the area's deep wells and evaluated nitrate $\delta^{15}N$ values in samples containing > 5 mg L^{-1} nitrate. Individual well waters had nitrate $\delta^{15}N$ values typical of animal waste sources (> 10‰), fixed N (-4‰ to +4‰), or mineralized soil organic N (+4‰ to +9‰) (Bahr and Carlson, 2000; Holloway et al., 2004; Unkovich, 2013). Groundwater nitrate ^{15}N and ^{18}O isotopes in 31 of the area's deep wells were evaluated from a single water sample collected in 2001; the author's concluded that denitrification was not a dominant process during nitrate transport (Tesch and Carlson, 2004). Plummer et al. (2000) reported that groundwater sampled in the area is nearly saturated with oxygen, which inhibits microbial denitrifier activity. A more frequent sampling of the tract's irrigation and shallow groundwaters, combined with stable isotope analysis is needed to improve our understanding of water and nitrate status there. For example, denitrification may vary with year or season and a single annual sample may not detect its occurrence.

The current research 1) evaluates the ^{15}N and ^{18}O isotopic signature of nitrate, and the deuterium (^{2}H) and the ^{18}O isotopes in irrigation water and subsurface tunnel drain outflow sampled in 2002–2007; and 2) determines the ^{15}N and ^{18}O isotopic signatures of fertilizer and manure nitrate sources, which are potential inputs and end members in the continuum. We hypothesized that 1) the transit time for water in shallow groundwater outflow from tunnel drains is relatively short (< 3 y); 2) stable isotope ratios of water and nitrate could be used to test our supposition that fixed-N is the primary source of leached nitrate; and 3) nitrification, not denitrification, is the dominant process in the nitrogen cycle in these agricultural soils.

2. Materials and methods

2.1. Study area

The Twin Falls Canal Co. irrigation tract is located in the Upper Snake River Basin of southern Idaho at an elevation of 884 to 1250 m (Fig. 1). Soils are dominated by Portneuf silt loam (coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcids) and Sluka silt loam (coarse-silty, mixed, superactive, mesic, Xerollic Haplodurids), which is similar to the deeper Portneuf except Sluka is moderately deep to a duripan. Shortly after the tract was developed, localized high water tables formed as a result of irrigation (Carter et al., 1971). Consequently, more than fifty drainage networks were constructed to alleviate saturated conditions. For each, a series of 9-to-21-m-deep relief wells were drilled vertically through the bedrock and intercepted at 1.1-to-12-m depth either by horizontal tunnels (1.2 × 2-m) blasted in the basalt bedrock or by tile drain piping (Carter et al., 1971; Cothern, 2013). Shallow groundwater is conveyed by gravity flow through individual networks and exits from outlets located in canyons or man-made surface drainage channels. Hence the groundwater draining from the networks, hereafter referred to as tunnel water, is a mixture of excess irrigation water draining from the soil above, and groundwater, which wells up in bore holes from bedrock below. The tract was described in detail by Carter et al. (1971). The study area includes the outlet drains monitored in 1968–70 by Carter et al. (1971) (Fig. 1). Agricultural crops and management practices of the study area were described by Lentz et al. (2018).

2.2. Sampling and analysis

We revisited and sampled 10 of the original 15 tunnel network drains evaluated by Carter et al. (1971) across the TFCC tract (Fig. 1). The 10 drains (Table 1) were stratified by area to ensure complete coverage of the study lands. Water samples were also collected at the Milner Dam pool (42°31′38″ N, 114°02′14″ W), which supplies water to the irrigation canals that convey the water downslope across the tract. Water samples for nutrient and isotope analysis were collected in 2003 through 2007 once per month during the April to November irrigation season, and on alternate months in the off season. Nutrient concentrations in these samples were analyzed and reported in a companion paper (Lentz et al., 2018). We sampled water (125 mL) from flows issuing directly from the tunnel drain outlet and stored it on ice until transported to the lab. Particulates present in water samples collected from tunnel drains, the Milner pool, and percolate from the laboratory experiment (see: Incubation Study) were removed by passing the liquid through a nitrate-free 0.45-μm filter. Of the sediment-free water sample, 20 mL was frozen in a scintillation vial for nitrate ^{15}N and ^{18}O isotope analysis and a 30-mL portion was stored at 4 °C for deuterium (^{2}H) and ^{18}O isotope analysis. Isotope samples were archived and selected sets were shipped for analysis beginning in 2005.

Water samples were shipped frozen on dry ice to the Marine Chemistry and Geochemistry Laboratory at Woods Hole Oceanographic Institution (Woods Hole, MA) for nitrate isotope analysis. The laboratory employed the microbial denitrifier method (McIlvin and Casciotti, 2011) and Gas Isotope Ratio Mass Spectrometry (Finnigan Delta^{PLUS} XP, Waltham, MA) to measure $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 (Eqs. (1) and (2)). The standard isotopic ratio for N was atmospheric N_2 (AIR) while that for O was the Vienna standard mean ocean water (VSMOW). Because the computed ratio is small, the value is multiplied by 1000 and reported per mil (‰):

$$\delta^{15}N\text{-}NO_3\ (‰) = \{[(^{15}N/^{14}N)_{sample}\ /(^{15}N/^{14}N)_{AIR}] - 1\} \times 1000 \quad (1)$$

$$\delta^{18}O\text{-}NO_3\ (‰) = \{[(^{18}O/^{16}O)_{sample}\ /(^{18}O/^{16}O)_{VSMOW}] - 1\} \times 1000 \quad (2)$$

where the sample N and O isotopes were determined from the nitrate in the water. Measurement precision was 0.1 to 0.2‰ for both $\delta^{15}N$ and $\delta^{18}O$ (McIlvin and Casciotti, 2011).

A subset of tunnel water and irrigation water samples were sent to the University of Arizona Environmental Isotope Laboratory (Tucson, AZ) where they were analyzed for $\delta^{2}H$-H_2O (Eq. 3) and $\delta^{18}O$-H_2O (Eq. 4). Waters were analyzed for D/H ratio using a dual inlet mass spectrometer (Delta-S, Thermo Finnegan, Bremen, Germany) equipped with an automated chromium reduction device (H-Device, Thermo Finnegan) for the generation of hydrogen gas using metallic chromium at 750 °C. Water $\delta^{18}O$ was measured on the same mass spectrometer using an automated CO_2-H_2O equilibration unit. Standardization is based on internal standards referenced to VSMOW. Precision is better than ± 0.1‰ for $\delta^{18}O$ and ± 1‰ for δD (1 sigma)..

$$\delta^{2}H\text{-}H_2O\ (‰) = \{[(^{2}H/^{1}H)_{sample}\ /(^{2}H/^{1}H)_{VSMOW}] - 1\} \times 1000 \quad (3)$$

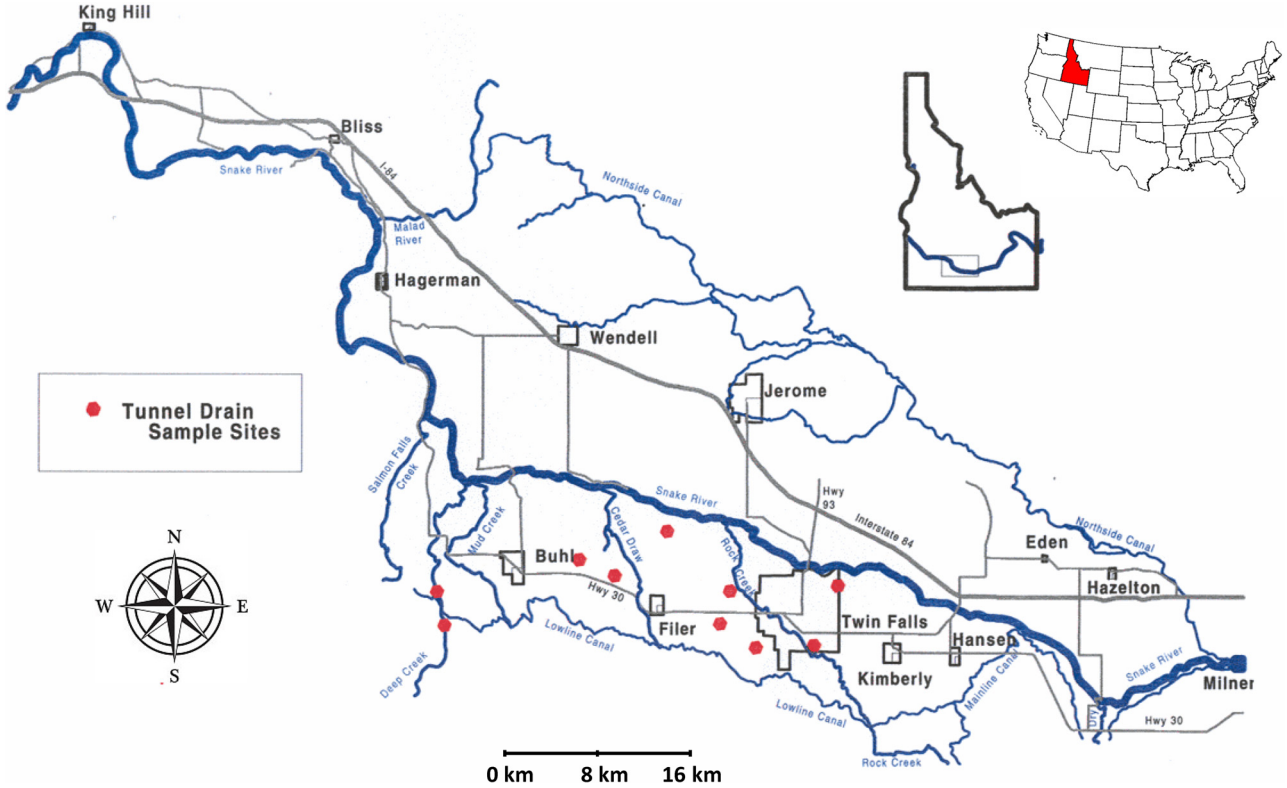

Fig. 1. Study area within Twin Falls Canal Co. Irrigation Tract in south-central Idaho and locations of sampled tunnel drains.

Table 1
Name and location of tunnel drains monitored in the study in the early-2000s, including land use and irrigation employed on land served by each, distance to the Snake R., elevation of tunnel outlet[§], and mean dissolved nitrate-N and phosphorus concentrations in tunnel water.

Tunnel Name	Location[†]	Land Use[‡]	Irrigation type used on land served by drain %	NO_3-N mg L^{-1}	PO_4-P µg L^{-1}	Distance to Snake R. km	Elev.[§] m
Cox	42° 34.05' N 114° 50.12' W	C	Furrow 100%	5.97	14.5	10.8	1128
CSI Fish Hatchery	42° 32.67' N 114° 27.84' W	R, P, F	Furrow 55%, Residential/Fallow 45%	3.54	16.1	6.1	1155
Grossman	42° 32.85' N 114° 30.34' W	P	Flood 100%	4.03	13.8	7.1	1177
Hankins	42° 35.10' N 114° 25.28' W	P, F, R	Furrow-Flood 48%, Sprinkler/Fallow 52%	5.18	7.6	1.7	1110
Harvey	42° 36.36' N 114° 42.53' W	C	Furrow 70%, Sprinkler 30%	5.16	18.4	6.5	1140
Herman (Dolan)	42° 32.99' N 114° 49.94' W	C, P	Furrow/Flood 75%, Sprinkler 25%	6.72	17.0	12.6	1158
Nye	42° 33.33' N 114° 31.54' W	C	Sprinkler 90%, Furrow 10%	4.58	7.2	6.9	1146
Peavy	42° 35.06' N 114° 39.14' W	P	Flood 100%	5.52	10.0	7.7	1138
Tolbert	42° 34.62' N 114° 31.28' W	C	Furrow 68%, Sprinkler 32%	5.16	7.5	4.8	1119
Walters	42° 37.74' N 114° 35.705' W	C, P	Furrow/Flood 100%	4.80	9.2	1.5	1079

[†] Uses WGS84/NAD83 datum.
[‡] C = cropped; F = fallow; Fl = flood irrigation; Fr = furrow irrigation P = pasture, R = residential, S = sprinkler irrigation.
[§] Elev. = the elevation of the tunnel outlet and can be compared to the elevation of the Snake River, which ranges in elevation from 900 to 960 m in the study area.

$$\delta^{18}O\text{-}H_2O\ (‰) = \{[(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{VSMOW}] - 1\} \times 1000 \quad (4)$$

where the H and O were measured in the sample water.

Due to expense, only 177 of the 460 water samples were selected for NO_3 and/or H_2O stable isotope analysis (112 for NO_3 and 99 for H_2O). For nitrate isotopes ($\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$), we selected 1) sample dates in 2003–2005 for the tunnel waters having the greatest NO_3-N concentrations (Herman) and two that had the least (Nye, College of southern Idaho [CSI] hatchery); 2) February, July, and September sample dates in 2005 through 2007 for all tunnel water samples (Table 1); and 3) irrigation water collected at the research farm near Kimberly, ID (42°31′04″ N, 114°22′20″ W) during the 2003–2004 growing seasons. For water isotopes ($\delta^2H\text{-}H_2O$, $\delta^{18}O\text{-}H_2O$),

Table 2
Pearson correlations and significance for normalized tunnel-water H_2O isotopes ($\delta^{18}O$- H_2O) vs. selected climatic and hydrologic parameters for all tunnel drains. The analysis evaluated the correlation of the H_2O isotope with climatic/hydrologic parameter values from the current-year, as well as one, two, and three years previous. (n = 98).

Paramete[†]	Expected Correlation[‡]	Pearson correlations and significance			
		Current Year	1-y previous	2-y previous	3-y previous
MAT	positive	−0.22 *	0.27 **	−0.05	−0.06
Wintr	positive	−0.15	0.30 **	−0.13	−0.21*
Sum	positive	−0.28 **	0.32 ***	0.10	0.07
Sumppt	positive	−0.22 **	0.39 ***	−0.21 *	−0.29 **
FlwMM	negative	−0.13	−0.22 *	−0.10	0.13

* Significant at the $P \leq 0.05$ probability level.
** Significant at the $P \leq 0.01$ probability level.
*** Significant at the $P \leq 0.001$ probability level.
[†] MAT = mean annual air temperature; Wintr = mean air temperature (Nov.–Feb. previous to growing season); Sum = mean air temperature (July-Sept.; Sumppt = summer precip. (July-Sep.); FlwMM = mean flowrate in Snake River in Mar., Apr., and May. Temperature and precipitation data were measured at Kimberly, ID; Snake R. flow was measured at Blackfoot, ID and was divided by its 1996–2011 flow mean.
[‡] The type of correlation expected if the tunnel water $\delta^{18}O$- H_2O is responding to effects of the climate/hydrologic parameter.

we selected 1) the sample dates in 2003–2004 for the CSI hatchery, Herman, and Walters tunnels; and 2) all sampling dates in 2006–2007 for Cox, Grossman, Herman, and Nye (Table 1), including the Milner dam pool. These tunnels represented sites having a range of irrigation types (Table 1) and NO_3-N concentrations.

2.3. Relating tunnel water $\delta^{18}O$-H_2O to climatic and hydrologic parameters

The $\delta^{18}O$-H_2O of precipitation is strongly influenced by temperature during rainout (Clark and Fritz, 1997). Thus, one can reasonably expect that the $\delta^{18}O$-H_2O of the Tract irrigation water, whose main source is precipitation falling on upstream mountains, is correlated with climatic parameters. Similarly, a correlation would be expected with certain hydrologic parameters, such as spring flowrate in the Snake R., which is largely controlled by snowmelt rates in upstream mountains. It follows that temporal origin of Snake R. irrigation recharge water supplying tunnel drains may be traced by comparing tunnel water $\delta^{18}O$-H_2O with current and past annual climatic or hydrologic parameters. Correlations between tunnel water $\delta^{18}O$-H_2O and annual climatic/hydrologic parameters from current and one, two, and three years previous (listed in Table 2) aided in estimating tunnel water transit time.

2.4. Incubation study

The objective of the experiment was to characterize the stable isotope status of nitrate in water leaching from agricultural soil amended with different N sources. These leached waters approximate a mixing end member series that contribute to the isotopic condition of the area's shallow groundwater (Kendall, 1998). Two N-sources were urea fertilizer, representing fixed-N, and dairy manure. The laboratory incubation study determined the nitrate ^{15}N and ^{18}O fractionation characteristics of water draining from un-amended, and urea fertilizer- or manure-amended soils. The experiment employed a completely randomized design, with three treatments and six replicates (18 experimental units). A 0–30 cm depth sample of Portneuf silt loam was collected, ambient nitrate was removed by extraction with reverse osmosis (RO) water, air dried, and sieved through a 2-mm screen. One of the following three amendment treatments was mixed with 125 g of soil: 1) 0.04 g total N as freeze-dried manure (6.74 g dairy manure, dry wt.); 2) 0.04 g N as urea fertilizer (0.1 g); or 3) no amendment.

The treated soil was packed into 13-cm long by 4-cm diameter PVC cylinders with nylon cloth (50 μm mesh) bottoms in three lifts to achieve a dry bulk density of about 1.15 Mg m^{-3}. Extra soil columns prepared for each treatment were used to determine soil pore volumes and track soil NO_3-N concentrations during incubation.

Soil in each cylinder was wetted to 55% water filled pore space (WFPS) using RO water and incubated at 22 °C. Soil water contents were adjusted to 55% WFPS weekly. All soil columns were leached after six months incubation, ensuring that the accumulated NO_3-N included an ample proportion of input N that had cycled through the soil system. For leaching, RO water was applied to the column's nylon cloth shielded soil surface at a rate of 6.0 mL h^{-1} (4.8 mm h^{-1}) until one pore volume of soil percolate was collected from each soil column. Samples of the accumulated water were prepared for $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 analysis as described above.

2.5. Three-source, linear mixing model

A simple linear mixing model with three sources (Phillips, 2001) was employed to estimate fractional nitrate contributions from conventional fertilizer (F_{Fixed}), manure (F_{Man}), and regional groundwater (F_{GW}), to tunnel water ($_{Tun}$) nitrate. The linear equations (Eqs. 5–7) defining the system are:

$$\delta J_{Fixed}\, F_{Fixed} + \delta J_{Man}\, F_{Man} + \delta J_{GW}\, F_{GW} = \delta J_{Tun} \quad (5)$$

$$\delta K_{Fixed}\, F_{Fixed} + \delta K_{Man}\, F_{Man} + \delta K_{GW}\, F_{GW} = \delta K_{Tun} \quad (6)$$

$$F_{Fixed} + F_{Man} + F_{GW} = 1 \quad (7)$$

where $J_x = \delta^{15}N$-NO_3 and $K_x = \delta^{18}O$-NO_3 for each source component and tunnel waters (Fixed, Man, GW, and Tun). The solution was calculated as $X = A^{-1}B$ where X is the 1 × 3 solution matrix (F_{Fert}, F_{Man}, F_{GW}), A^{-1} is the inverse of the 3 × 3 source coefficient matrix, and B is the 1 × 3 tunnel results matrix. The model assumes that nitrate-N in waters is conservative, e.g. denitrification is a minor influence in the system; only three sources are contributing nitrate to tunnel water; and source (end-members) isotope compositions are constant.

2.6. Statistical analysis

Descriptive statistics (mean, standard deviation) for tunnel sample nitrate and water isotopes were obtained using PROC Mean (SAS, 2012) and tests for normality using PROC Univariate (SAS, 2012). The $\delta^{2}H$-H_2O, and $\delta^{18}O$-H_2O values for tunnel water and irrigation water were plotted relative to the local meteoric water line for southeastern Idaho and regression lines were fitted to irrigation water data using PROC Reg (SAS, 2012).

We employed Pearson's correlations calculated by PROC Corr (SAS, 2012) to evaluate the relationships between normalized tunnel water $\delta^{18}O$-H_2O values vs. selected climate and hydrologic parameters for current and one, two, and three years previous. Tunnel water $\delta^{18}O$-H_2O values were normalized by dividing each by its tunnel mean. The

analysis included available isotope data from all tunnel drains for years 2003 to 2007. In another analysis, correlations were determined between tunnel drain location (distance to the Snake R.) and each of the following tunnel water traits, nitrate concentration, δ^{15}N-NO_3, δ^{18}O-NO_3, δ^{18}O-H_2O, and δ^{2}H-H_2O.

To determine if δ^{15}N-NO_3 and δ^{18}O-NO_3 compositions differed among the tunnel water and incubation treatment leachate (endmember series) we conducted an analysis of variance (ANOVA) using PROC MIXED (SAS, 2012) with water source group as the fixed effect and year and year*group as random effects. Then 95% confidence limits were constructed on treatment means. A similar approach was used to determine if the δ^{15}N-NO_3, δ^{18}O-NO_3, δ^{2}H-H_2O, or δ^{18}O-H_2O, ratios differed between the group of three tunnel waters that had the greatest nitrate concentration relative to the group of three having the least (Table 1).

The alignment and variance associated with δ^{15}N-NO_3 and δ^{18}O-NO_3 values from tunnel waters and the end member series were plotted for comparison using the following two-step process. The δ^{15}N-NO_3 and δ^{18}O-NO_3 values were plotted separately for control-, Urea-, and manure-soil endmembers, Hankins and Walters tunnel waters, combined, and all-other tunnel waters combined. A line intersecting each group's spatial mean was drawn parallel to the group's long axis of symmetry, i.e. in the direction of greatest spatial spread among data points. A second shorter line, representing short axis of symmetry was drawn, also intersecting the spatial mean but perpendicular to the first. We then quantified the amount of spread among the group's data points in the long- and short symmetry-axis directions. This was accomplished by rotating and aligning the X–Y coordinate axes with the group's long and short symmetry axes, transforming the group's point coordinate values relative to the new coordinate axes, then computing standard deviations for the transformed x and y coordinate values (See Fig. 7).

3. Results and discussion

3.1. Irrigation and tunnel water ^{2}H and ^{18}O

Milner irrigation and tunnel water δ^{2}H-H_2O and δ^{18}O-H_2O values overlap, indicating that irrigation water is an important source of recharge for shallow ground water (Fig. 2). Milner waters plot close to the local meteoric water line (LMWL) (Cecil et al., 2005). Milner and tunnel water δ^{2}H-H_2O and δ^{18}O-H_2O values are smaller in comparison to late spring, summer, and fall meteoric waters, which lie outside plot area in Fig. 2 and typically have δ^{18}O-H_2O values greater than -15.5‰ (Benjamin et al., 2004). Precipitation becomes depleted in ^{2}H and ^{18}O as cloud temperature decreases in response to seasonal or elevation-related effects. Hence, meteoric water, and dominantly winter precipitation (snow) is the ultimate source of Milner and tunnel water.

The slopes of regression lines fitted to data from Milner dam pool for 2006 (4.8) and 2007 (5.4) data are typical for surface water under evaporative regimes, which commonly range from 4 to 6 (Barnes and Allison, 1988; Clark and Fritz, 1997). Milner irrigation water becomes isotopically enriched during nonequilibrium evaporation from reservoirs, canals, and soils, which results in a positive shift in plotted points and a decrease in plot slopes (Clark and Fritz, 1997; Benjamin et al., 2004). Because 2007 was substantially warmer and dryer than 2006, with greater evaporation, the Milner 2007 regression line is displaced further from the LMWL (Clark and Fritz, 1997). Furthermore, the correspondence of irrigation and tunnel water plots in the upper-right range for Milner water indicates that these shallow groundwaters are primarily recharged by irrigation water applied during the growing season (Figs. 2 and 3).

Regional groundwater is another potential recharge source for the shallow groundwater. The former originates in mountains to the south of the tract and is less affected by evaporation (Plummer et al., 2000). Therefore, the regional groundwater can be more depleted in δ^{2}H-H_2O, and δ^{18}O-H_2O than Milner water (Fig. 2).

3.2. Transit time

The δ^{18}O-H_2O time series from Milner pond and select tunnel drains (2006, 2007) displayed in Fig. 3 and correlations of tunnel water δ^{18}O-H_2O with current and previous year's climate/hydrologic parameters in Table 2 were used to estimate the time required for water applied at the soil surface to transit to the shallow aquifer (Ingraham et al., 1991). Cool-season precipitation and snowmelt runoff contribute water depleted in heavy isotopes to the Milner reservoir, which produces a decline in δ^{18}O-H_2O values, attaining a minimum in early to late spring (Fig. 3C). During the growing season, reservoir inflows are more heavily influenced by seepage, spring, irrigation return, and reservoir storage waters, which are enriched in heavy isotope concentrations due to evaporation. This causes a rise in δ^{18}O-H_2O values, peaking in early to late fall (Fig. 3C).

Smaller scale variations in the pattern likely result from annual variations in climate and hydrology (Fig. 3C). For example, 2006 was unusually wet and cool with a heavy snowpack that produced increased summer reservoir levels, whereas antithetical weather in 2007 produced decreased summer reservoir levels (Fig. 3A, B). The diminished contribution of precipitation and runoff to the reservoir in 2007 increased the proportion of shallow groundwater seepage contributions and contracted the range of δ^{18}O-H_2O values observed relative to 2006 (Fig. 3C).

The lag time between the seasonal δ^{18}O-H_2O peaks in Milner irrigation water and subsequent peaks in tunnel drain water varied between 8 and 11 months (Fig. 3C). The period measured for some tunnels may differ from the actual value by up to 2 months because water was sometimes sampled on alternate months, particularly outside the growing season. In some cases, the lag varied 1) between tunnel drains, presumably due differences in local hydrogeology, and 2) between years for the same tunnel drain, possibly due to differences in crops grown between years and hence the amount and timing of irrigation water applied. The differences in lag were not considered conclusive due to the timing of sample collection.

Because Milner δ^{18}O-H_2O peaks occur annually, tunnel water δ^{18}O-H_2O peaks in the current year may represent the arrival of the most recent Milner peak water, or the arrival of Milner peak water from one, two, or three years previous. Given that tunnel water δ^{18}O-H_2O values are correlated most strongly and significantly with climate/hydrologic parameters from one year previous (Table 2), we conclude that the Milner and tunnel water signals are one year out of phase. This suggests that the transit time between the surface and shallow groundwater is between 20 and 23 months. Others have estimated transit times for shallow groundwaters (< 10-m depth to water) to be 1.2 y in glacial till; < 5 y in layered sediments; ≤ 3 y in loamy sands, or 4 y in alluvial fill sediments (Reddy et al., 2006; Moore et al., 2006; Turkeltaub et al., 2016).

The 20-to-23-month transit time is very short relative to that estimated for deep groundwater in the area, tens or hundreds of years (Mann and Low, 1994). This implies that the chemistry of the deep groundwater source has not yet fully absorbed the impact of the post-1960s expansion in inorganic and organic fertilizer use by agriculture in the Twin Falls tract (Lentz et al., 2018). The shallow groundwater responds far sooner, which ostensibly is the reason why mean tunnel water nitrate-N concentrations have risen 1.4-fold, from 3.6 to 5.1 mg L^{-1}, between the late-1960s and early 2000s (Lentz et al., 2018). Notably, this 1.4-fold increase in tunnel-water nitrate concentration appears modest compared to the concomitant 2.2-fold increase in fertilizer applications in the tract (Lentz et al., 2018).

3.3. Tunnel water δ^{15}N-NO_3, δ^{18}O-NO_3

On the whole, tunnel water nitrate δ^{15}N-NO_3 values ranged from +4.6‰ to +7.8‰ and δ^{18}O-NO_3 ranged from -4.5‰ to -7.6‰. Generally tunnel water δ^{18}O-NO_3 values present a bimodal pattern,

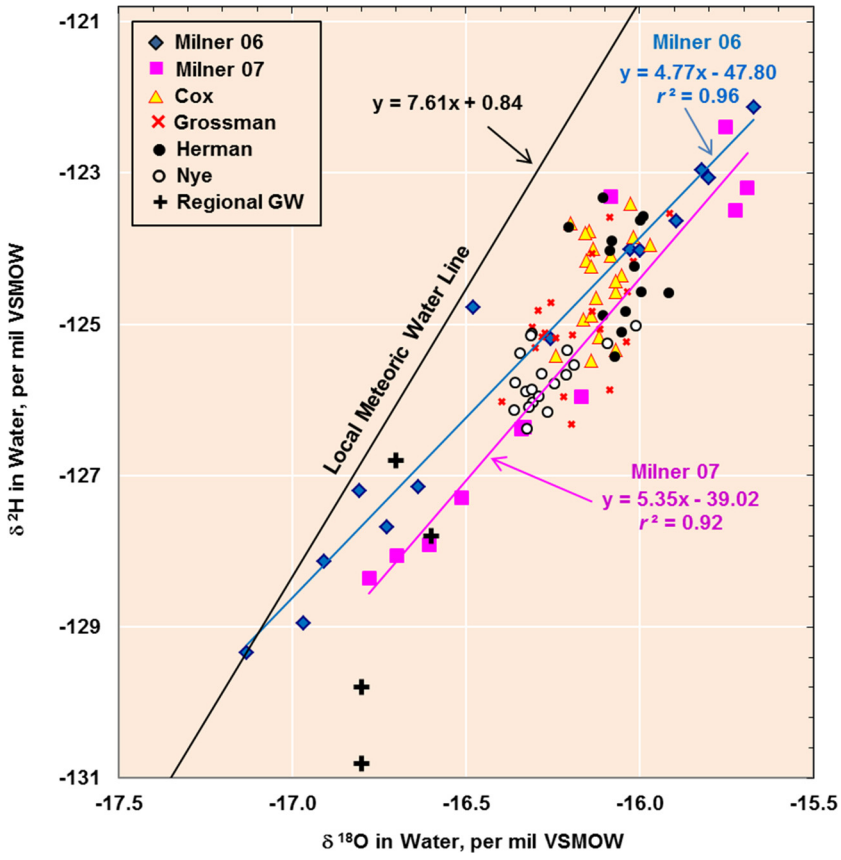

Fig. 2. Stable isotope composition of Cox, Grossman, Herman, and Nye tunnel waters; irrigation water in 2006–2007; and regional groundwater (GW) (Source: Young and Lewis, 1980; Lewis and Young, 1982) compared with seasonal variation of the Local Meteoric Water Line (LMWL) for southeastern Idaho (Source: Cecil et al., 2005).

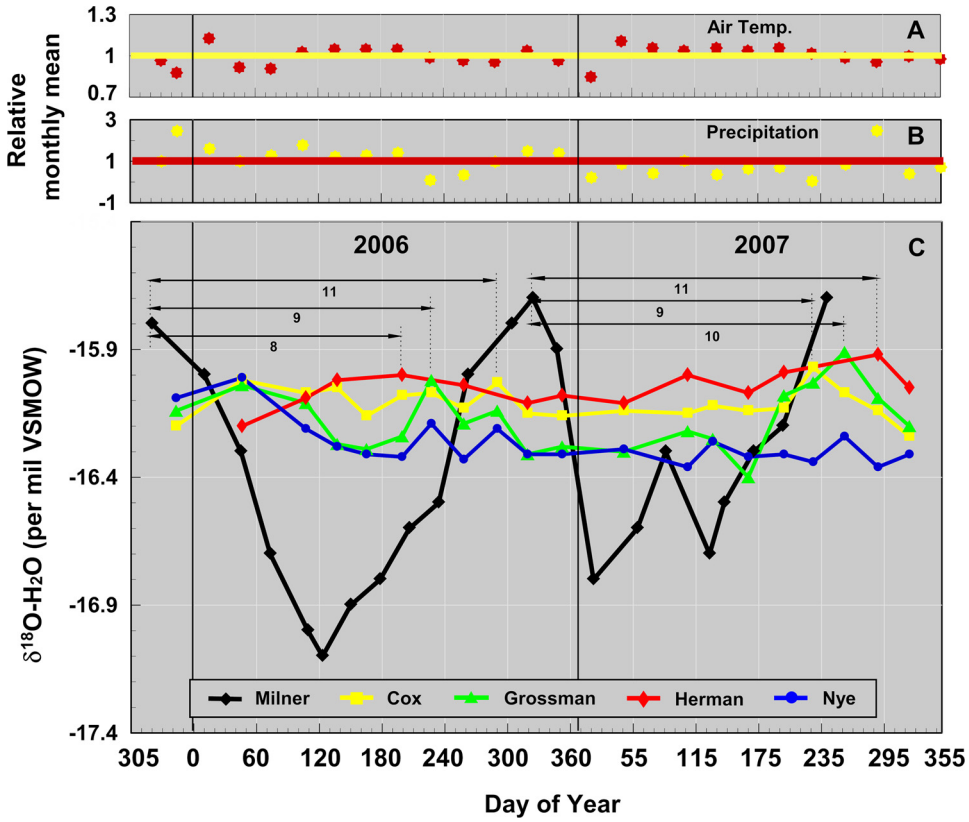

Fig. 3. For years 2006 and 2007, monthly air temperature (A) and precipitation (B) values given as the relative mean (monthly mean/1996–2016 monthly mean), and Milner pond (irrigation source) and tunnel water $\delta^{18}O$-H_2O values (C), are plotted as a function of day of year. Lag times between irrigation and tunnel $\delta^{18}O$-H_2O peaks are shown in month units.

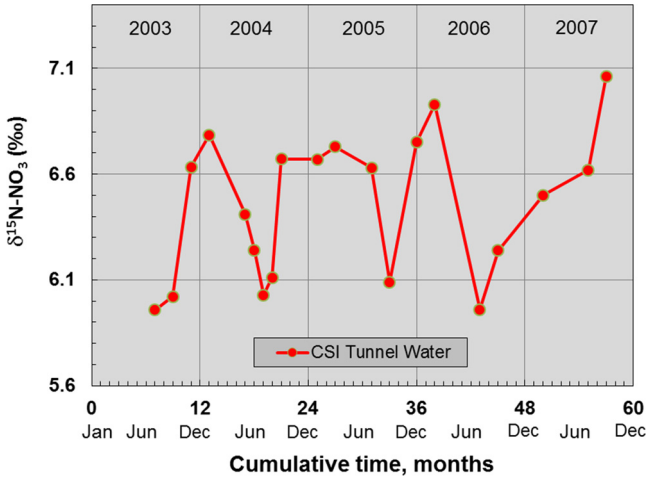

Fig. 4. Time series of CSI Hatchery Tunnel nitrate δ15 N-NO3 for 2003 through 2007.

with δ^{15}N-NO_3 cycling from low values during the mid to late summer to higher values in winter. Data from the most frequently sampled tunnel, CSI hatchery, illustrates the pattern (Fig. 4). A similar bimodal pattern was observed in deep (1.2 m) percolation water in Portneuf soils (Lentz and Lehrsch, 2018) and other soils (Ostrom et al., 1998; Loo et al., 2017) except the peak occurs in late summer or fall. The percolating water recharges shallow groundwater and is the source of seasonal δ^{15}N-NO_3 fluctuations.

3.4. The relation between drain location and tunnel-water stable isotopes and nitrate

When tunnel water δ^{15}N-NO_3 and δ^{18}O-NO_3 values from Jan., July, and Sep. (or two of the three) are plotted for 2005, 2006, and 2007, the tunnel groups sort into a linear pattern in any given year. That is, the δ^{15}N-NO_3 and δ^{18}O-NO_3 of waters from individual tunnels tend to increase along a line, with Walters and Hankins having the smallest values, CSI moderate, and Herman and Grossman being largest (Fig. 5). This is particularly striking in 2007 data (Fig. 5C). Could the pattern be related to tunnel location? Pearson's analysis showed that tunnel water

Table 3
Pearson's correlations and significance of tunnel drain location, given as the distance to the Snake R., with tunnel water NO_3-N concentrations, and NO_3 and H_2O stable isotopes, for years 2005, 2006, and 2007.

Year	NO3-N	δ^{15}N- NO_3	δ^{18}O- NO_3	δ^{18}O- H_2O	δ^{2}H- H_2O
2005	0.32**	NS†	0.67***	-‡	–
2006	0.62***	0.61 **	0.81***	0.62***	0.75***
2007	0.64***	0.67 ***	0.84***	0.64***	0.49**

** Significant at the $P \leq 0.01$ probability level.
*** Significant at the $P \leq 0.001$ probability level.
† NS = nonsignificant ($P > 0.05$).
‡ Insufficient data.

δ^{15}N-NO_3, δ^{18}O-NO_3, δ^{2}H-H_2O, and δ^{18}O-H_2O values are positively correlated with tunnel drain location, given as its distance to the Snake R. in the direction of groundwater flow (Table 1 and 3). Thus, the fractions of heavy isotopes in the tunnel water decline as distance to the river and elevation decrease. Because decreasing tunnel water and nitrate heavy-isotope fractions are associated with a shift toward regional groundwater (Fig. 2, Section 3.6), it would appear that the contribution of regional groundwater to tunnel water increases towards the Snake R. (Plummer et al., 2000), and results in the linear pattern seen in Fig. 5. The positive correlation between tunnel water NO_3-N concentration and the tunnel-Snake R. distance is consistent with this scenario (Table 3). The increased contribution of nitrate-poor regional groundwater to the shallow groundwater, relative to contributions of nitrate-rich soil percolation water, would dilute NO_3-N concentrations.

3.5. Tunnel Water δ^{15}N-NO_3 vs. δ^{18}O-NO_3 distribution

The plot of stable isotope values from all tunnel water samples showed a relatively scattered distribution, but revealed a significant positive relationship between δ^{15}N-NO_3 and δ^{18}O-NO_3 ($P < 0.0001$) (Fig. 6A). A nearly 2:1 ratio of δ^{15}N-NO_3 to δ^{18}O-NO_3 like that observed for the tunnel water (Fig. 6A) is often taken as an indicator of denitrification (Bottcher et al., 1990; Kaushal et al., 2011). However, Bottcher et al.'s (1990) data set included groundwater samples with δ^{15}N-NO_3 values ranging from 9‰ to 78‰ compared to a range of 4.5‰ to 7.5‰ in the current study. When Portneuf soils were incubated under saturated conditions, residual nitrate δ^{15}N-NO_3 values

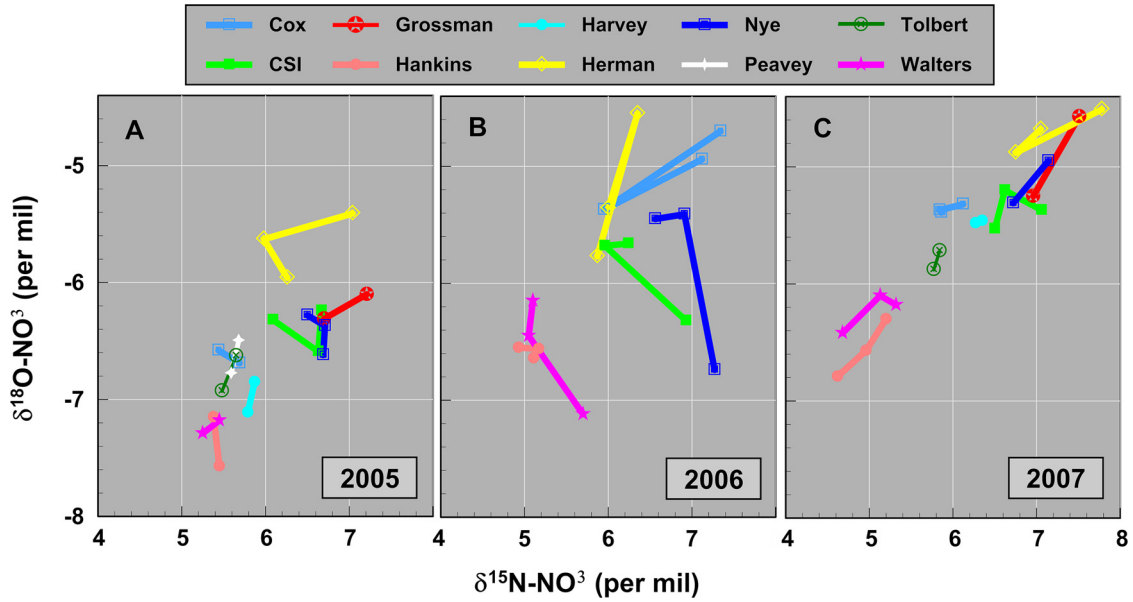

Fig. 5. Dual tunnel water δ^{18}O-NO_3 and δ^{15}N-NO_3 plots for individual tunnel drains in January, July, and September (or two of the three) of 2005 (A), 2006 (B), and 2007 (C).

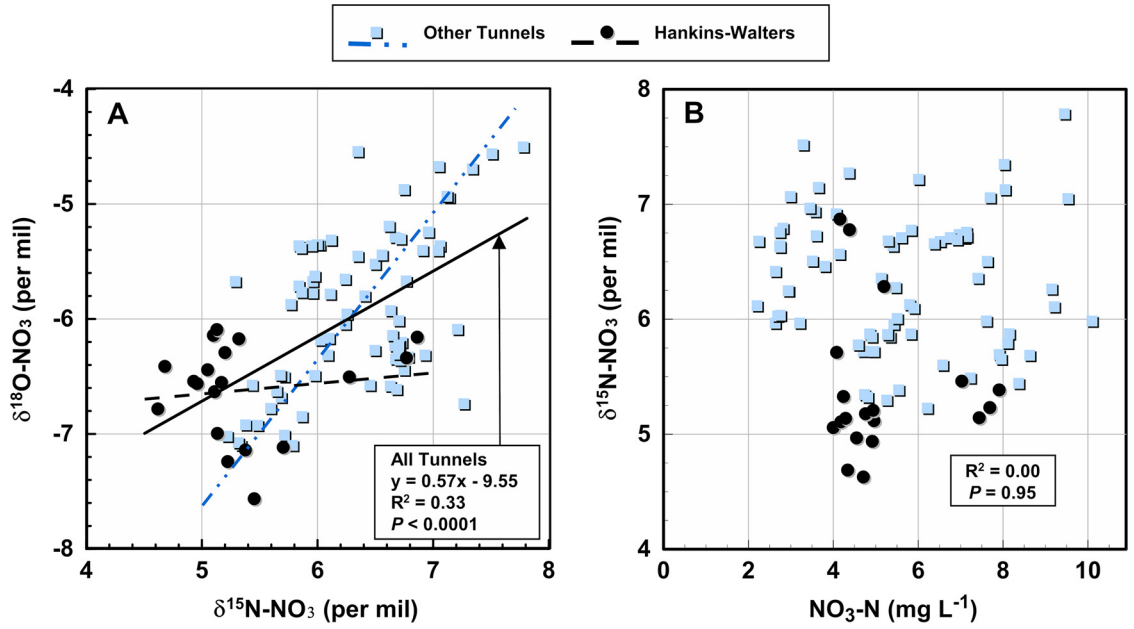

Fig. 6. (A) Overall relationship between tunnel water δ^{15}N-NO_3 and δ^{18}O-NO_3 for 2003 through 2007 (solid line). Dashed lines represent the direction of greatest spatial spread in data (long axis) for Hankins and Walters combined, and all-other tunnel drains combined. (B) Overall relationship between tunnel water nitrate concentration and δ^{15}N-NO_3.

ranged from 12‰ to 38‰ (unpublished data). Bottcher et al.'s (1990) data also revealed an inverse relationship between nitrate concentration and δ^{15}N-NO_3, which was not seen in tract tunnel waters (Fig. 6B). This argues against denitrification as an dominating influence in the system (Mariotti et al., 1988; Kendall, 1998).

Alternatively, the linear relationship (Fig. 6, All tunnels) may be the result of mixing with regional groundwater (Fig. 7 and Section 3.6) This view is consistent with 1) a field study in Portneuf soils that analyzed nitrate and δ^{15}N-NO_3 in percolation water at 1.2-m-depth, concluding that denitrification was not a dominant process in the soils (Lentz and Lehrsch, 2018); 2) reports that area groundwaters are fully oxygenated (Plummer et al., 2000); and 3) isotope studies in free-draining soils that commonly find little evidence of denitrification (Ostrom et al., 1998; Smith and Kellman, 2011; Kelley et al., 2013).

Note also in Fig. 6A that Hankins and Walters ^{15}N-NO_3 values were in the lower range of all tunnels, and δ^{18}O-NO_3 values showed the least variation relative to all-other tunnels.

3.6. Comparing incubation end-members and tunnel waters (δ^{15}N-NO_3, δ^{18}O-NO_3)

The urea-soil and manure-soil endmember isotope compositions were enriched in δ^{18}O-NO_3 (+2.2‰) relative to the control-soil (Fig. 7, Table 4). This resulted from microbial nitrification of source-derived NH_4-N to NO_3-N (Kendall, 1998; Nestler et al., 2011). The δ^{18}O-NO_3 ratio for both endmembers was −4.7‰. From the equation: $\delta^{18}O\text{-}NO_3 = NR{\cdot}\delta^{18}O\text{-}H_2O + (1\text{-}NR){\cdot}\delta^{18}O\text{-}O_2$; where $\delta^{18}O\text{-}H_2O = -16.5‰$ (estimated from Fig. 2) and $\delta^{18}O\text{-}O_2 = +23‰$ (the value for atmospheric O_2 presumed unfractionated when dissolved in soil H_2O, Clark and Fritz, 1997), the nitrification ratio (NR) is calculated as 0.70. Hence the fraction of O contributed from irrigation-H_2O O during nitrification was 0.70 and the fraction contributed from soil gaseous O_2-O was 0.30. This contribution of O from water is slightly higher than that commonly cited (0.67, Hollocher, 1984; Shalev et al., 2015), but lower than that observed by Snider et al. (2010), who reported fractional H_2O-O contributions during nitrification of 0.79 to 0.96.

The δ^{15}N-NO_3 ratio of the urea-soil endmember, +4.6‰ (Fig. 7), is enriched relative to the δ^{15}N of urea-N, which averages −0.2‰ (Kendall, 1998; Craine et al., 2015). This enrichment occurs in a matter of days in these soils. Lentz and Lehrsch (2018) reported that nitrate leached from Portneuf soil 48 h after urea application had a δ^{15}N-NO_3 of +4.6‰ and δ^{18}O-NO_3 of +7.1‰. Presumably the rapid enrichment results primarily from volatilization of urea-derived NH_4-N to NH_3-N and subsequent nitrification of the remaining NH_4-N (Nestler et al., 2011). Relative to the control- and urea-soil endmember, the manure-soil was enriched in δ^{15}N-NO_3 (+8.8‰, Table 4) owing to 1) discrimination and fractionation of N occurring during animal metabolic processes; and 2) volatilization of ammonia from excreted feces, followed by nitrification in the soil (Dittert et al., 1998).

The δ^{15}N-NO_3 and δ^{18}O-NO_3 ratios of Hankins-Walters and all-other tunnel waters were enriched compared to the control soil and deep groundwater endmembers (Table 4, Fig. 7). The Hankins-Walters tunnel waters were intermediate between all-other tunnels and the deep groundwater (Fig. 7), which suggests that shallow groundwater at locations nearer the Snake R. were more heavily influenced by recharge from deep groundwater. The greater contribution of regional groundwater to Hankins-Walters tunnel waters relative to all others 1) is consistent with the reduced temporal variability in δ^{18}O-NO_3 we observed for this group (Fig. 6A); and 2) may result from a relative paucity of soil water percolation at these sites.

These data indicate that tunnel water δ^{15}N-NO_3 and δ^{18}O-NO_3 values result primarily from the mixing of two end-member source waters, fixed-N (urea models NO_3-N nitrified from fertilizer and legume-residue) and manure-amended soil, with regional groundwater. The dual isotopic element, three-source, simple linear mixing model (Phillips, 2001) estimated the proportion of nitrate contributed from the three sources. On average, nitrate from Hankins-Walters tunnel waters was derived from 71% regional groundwater, 17% fixed-N, and 11% animal waste sources. Nitrate from all-other tunnel waters was derived from 47% regional groundwater, 32% fixed-N, and 21% animal waste sources. For both tunnel groupings, 1.5-times more nitrate is derived from fixed-N than animal waste sources. Thus, both fixed-N and animal waste sources contribute to the shallow groundwater nitrate concentration in the tract, though the larger share is from fixed-N sources.

3.7. Source of increased nitrate in shallow groundwater

Of the ten tunnels sampled, the three with the least outflow nitrate-

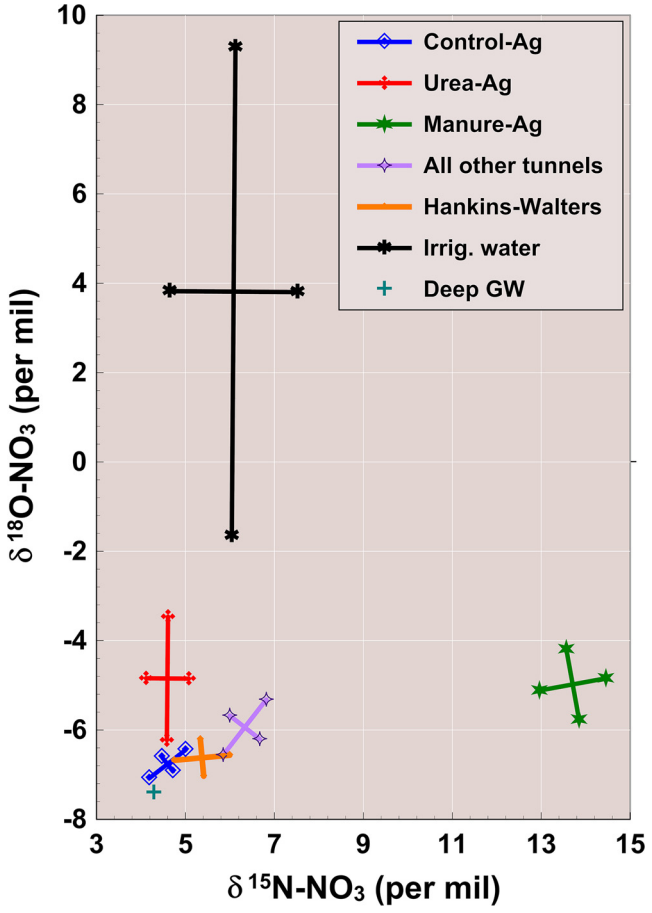

Fig. 7. Dual water δ^{18}O-NO_3 and δ^{15}N-NO_3 source distribution plots for: 1) non-treated (control), urea- or manure-amended soils (Incubation study); 2) shallow groundwater sampled from Hankins and Walters tunnel drains, combined vs. all-other drain waters; and 3) deep ground water (Deep GW). The error bars are the means ± 1 standard deviation obtained parallel and perpendicular to the direction of greatest spatial spread (long axis) for each data set.

Table 4
Effect of water source on δ^{15}N-NO_3 and δ^{18}O-NO_3 isotope ratios. Also shown are tunnel group and endmember stable isotope mean, minimum, maximum, and SE for each ratio.

	Analysis of variance (*P*-values)							
Source of variation	δ^{15}N-NO_3				δ^{18}O-NO_3			
Water Source	***				***			
Water Source	Source means, min., max., and se							
	Mean ‰	Min.	Max.	SE	Mean ‰	Min.	Max.	SE
All-Other Tunnels	6.3 b	5.2	7.8	0.07	−5.9 b	−7.1	−4.5	0.08
Hankins-Walters	5.4 c	4.6	6.9	0.14	−6.6 b	−7.6	−6.1	0.09
Endmember								
Control-Soil	4.6 d	4.2	5.1	0.16	−6.8 c	−7.3	−6.3	0.16
Urea-Soil	4.6 d	4.1	5.2	0.20	−4.9 a	−6.2	−2.9	0.56
Manure-Soil	13.4 a	11.3	14.7	0.51	−4.4 a	−5.7	−2.3	0.49

*** Significant at the P ≤ 0.001 probability level.

N concentrations (CSI, Grossman, and Nye) averaged 4.05 mg L^{-1}, while the three with the greatest nitrate concentrations (Cox, Herman, and Peavy) averaged 6.07 mg L^{-1} (Table 1). For these groups, the shift to greater outflow nitrate concentrations was accompanied by a decrease in δ^{15}N-NO_3 from 6.6‰ to 6.1‰, with little change in δ^{18}O-NO_3 (Table 5). The shift in the δ^{15}N-NO_3 towards that of the urea endmember value, 4.6‰ (Table 4) as nitrate concentration increases is evidence that the source of leached nitrate in shallow groundwater is fertilizer or fixed N from legume crops.

Table 5
Effect of tunnel water nitrate concentration (Nclass†) on δ^{15}N-NO_3, δ^{18}O-NO_3, δ^{18}O-H_2O, and δ^{2}H-H_2O isotope ratios. Significance *P*-values resulting from analysis of variance and Nclass mean values.

Analysis of Variance				
Source of variation	δ^{15}N-NO_3	δ^{18}O-NO_3	δ18O-H2O	δ2H-H2O
	P-values			
Nclass	*	0.68	*	**
	Nclass means			
Nclass†	‰	‰	‰	‰
Low nitrate	6.6 a	−5.8 a	−16.1 b	−126 b
High nitrate	6.1 b	−5.9 a	−16.0 a	−125 a

† The low nitrate Nclass included the three tunnels (CSI, Grossman, and Nye) with the least sample nitrate concentrations, and high Nitrate Nclass included the three tunnels (Cox, Herman, and Peavy) with the greatest nitrate concentrations.
* Significant at the $P \leq 0.05$ probability level.
** Significant at the $P \leq 0.01$ probability level.

The shift to greater tunnel nitrate concentrations was also associated with the enrichment of tunnel water δ^{18}O-H_2O and δ^{2}H-H_2O ratios (Table 5 and Fig. 2). This suggests that higher nitrate loads result in part, from a decrease in the regional aquifer contribution to the shallow groundwater, relative to that of infiltrating local irrigation water (Clark and Fritz, 1997; Plummer et al., 2000; Palmer et al., 2007).

4. Conclusions

1) Results support the hypothesis that transit time to shallow groundwater (tunnel outflows) is relatively short in the Twin Falls Irrigation Tract. Based on a time-series analysis of δ^{18}O ratios in tunnel-drain and irrigation water and correlation analysis (climatic/hydrologic parameters vs. Tunnel water δ^{18}O-H_2O values), we estimated transit times to be 20–23 months.
2) Stable Isotope ratios of the nitrate in tunnel outflow relative to that of urea fertilizer- and manure-amended soil nitrate sources suggest that nitrate in shallow groundwater is a function of nitrate leaching loads from local agricultural soils and dilution resulting from regional groundwater contributions. Note that urea and ammonium fertilizers comprised 90% of the total N fertilizer applied in the tract at the time of sampling.
3) The source of increased nitrate loads in tunnel outflows is a combination of animal waste and N derived from atmospheric N_2, including urea and ammonium fertilizer and N fixed by legumes. A mixing model indicated that, on average, 1.5X more N is sourced from fertilizer and fixed N than animal waste. The +0.6‰ enrichment in δ^{15}N-NO_3 and +1.0‰ enrichment in δ^{2}H-H_2O in water from tunnels having the least nitrate concentrations relative to those with the greatest concentrations further suggests that increased nitrate contamination results from increased contribution from fertilizer/fixed-N sources and reduced contribution of regional groundwater (less dilution).
4) The limited breadth of variation and lack of strong enrichment observed in tunnel water δ^{15}N-NO_3 values, combined with the absence of an inverse relationship between tunnel-water nitrate concentration and δ^{15}N-NO_3 suggest that denitrification has relatively minor influence on nitrate in the vadose zone and shallow groundwater of the tract. The dominant N cycling processes in these soils is the mineralization of soil organic matter and the nitrification of NH_4-N

derived from applied fertilizer and manure.

5) Presumably, the nitrate concentration in the deep groundwater of the tract will increase with time as it slowly comes into equilibrium with effects of post-1960s expanded fertilizer use. Since the deep water is an important contributor to shallow groundwater in the tract, these increasing nitrate loads could 1) increase shallow groundwater nitrate contamination; and/or 2) limit the effectiveness of any improved N management practices that are applied in the near future.

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